

IPEA/ EP

Rec'd PCT/PTO 22 JUL 2004

10/502267

PCT

CHAPTER II

DEMAND

under Article 31 of the Patent Cooperation Treaty:

The undersigned requests that the international application specified below be the subject of
international preliminary examination according to the Patent Cooperation Treaty

| For International Preliminary Examining Authority use only | | |
|--|---|--|
| Identification of IPEA | Date of receipt of DEMAND | |
| Box No. I IDENTIFICATION OF THE INTERNATIONAL APPLICATION | | Applicant's or agent's file reference 14128/WO/02 |
| International application No. PCT/IL03/00058 | International filing date (day/month/year) 23 January 2003 (23.01.2003) | (Earliest) Priority date (day/month/year) 31 January 2002 (31.01.2002) |
| Title of invention PENTABROMOBENZYL ALKYL ETHERS AND THEIR USE AS FIRE RETARDANTS | | |
| Box No. II APPLICANT(S) | | |
| Name and address: BROMINE COMPOUNDS LTD. Makleff House P.O. Box 180 Beer-Sheva 84101 Israel | | Telephone No : |
| | | Facsimile No : |
| | | Teleprinter No : |
| State (i.e. country) of nationality: IL | | State (i.e. country) of residence: IL |
| Name and address: ZILBERMAN, Joseph 13/2 Bat Chen Street Haifa 32990 Israel | | |
| State (i.e. country) of nationality: IL | | State (i.e. country) of residence: IL |
| Name and address: TAVOR, Alon 111 Eucalyptus Street Omer 84965 Israel | | |
| State (i.e. country) of nationality: IL | | State (i.e. country) of residence: IL |
| <input checked="" type="checkbox"/> Further applicants are indicated on a continuation sheet | | |

Continuation of Box No. II APPLICANT(S)

If none of the following sub-boxes is used, this sheet is not to be included in the demand.

Name and address:

CANFI, Dorit
61 Netiv Chen Street
Neve Sha'anana
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State (i.e. country) of nationality: IL

State (i.e. country) of residence: IL

Name and address:

IOFFE, David
46/19 Gut Levin Street
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State (i.e. country) of nationality: IL

State (i.e. country) of residence: IL

Name and address:

TITELMAN, Grigory I.
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Haifa 33061
Israel

State (i.e. country) of nationality: IL

State (i.e. country) of residence: IL

Name and address:

BRON, Samuel
11/1 Achziv Street
Yoqneam 20692
Israel

State (i.e. country) of nationality: IL

State (i.e. country) of residence: IL

 Further applicants are indicated on another continuation sheet.

Continuation of Box No. II APPLICANT(S)*If none of the following sub-boxes is used, this sheet is not to be included in the demand.*

Name and address:

WEINBERG, Olga
18/23 Abba Hiller Silver Street
Haifa 32694
Israel

State (i.e. country) of nationality: IL

State (i.e. country) of residence: IL

Name and address:

State (i.e. country) of nationality:

State (i.e. country) of residence:

Name and address:

State (i.e. country) of nationality:

State (i.e. country) of residence:

Name and address:

State (i.e. country) of nationality:

State (i.e. country) of residence:

 Further applicants are indicated on another continuation sheet.

Box No. III AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE

The following person is agent common representative

and has been appointed earlier and represents the applicant(s) also for international preliminary examination.

is hereby appointed and any earlier appointment of (an) agent(s)/common representative is hereby revoked.

is hereby appointed, specifically for the procedure before the International Preliminary Examining Authority, in addition to the agent(s)/common representative appointed earlier.

Name and address:

LUZZATTO, Kfir; LUZZATTO, Edgar; LUZZATTO, Esther; HACKMEY, Michal;
 FUERST, Zadok; MANZUROLA, Emanuel; CHECHIK, Haim; SERUYA, Yehuda;
 ZRIHAN-LICHT, Sheila; JACOBSON, Zvi-Michael; GUTTMANN, Thomas; ALPERT,
 Bruce; CROITORO, Boaz; WEISS, Shmuel; PRICE, Eyal; SHALEV, Ronit; HACKMEY,
 Miriam
 LUZZATTO & LUZZATTO
 P.O.Box 5352
 Beer-Sheva 84 152
 Israel

Telephone No :

(972-8) 646-7070

Faximile No :

(972-8) 646-7080

Teleprinter No.:

Mark this check-box where no agent or common representative is/has been appointed and the space above is used instead to indicate a special address to which correspondence should be sent.

Box No. IV STATEMENT CONCERNING AMENDMENTS

The applicant wishes the International Preliminary Examining Authority*

- to start the international preliminary examination on the basis of the international application as originally filed.
- to take into account the amendments under Article 34 of
 - the description (amendments attached).
 - the claims (amendments attached).
 - the drawings (amendments attached).
- to take into account any amendments of the claims under Article 19 filed with the International Bureau (a copy is attached).
- to disregard any amendments of the claims made under Article 19 and to consider them as reversed.
- priority that to postpone the start of the international preliminary examination until the expiration of 20 months from the date unless that Authority receives a copy of any amendments made under Article 19 or a notice from the applicant he does not wish to make such amendments (Rule 69 1(d)).

* Where no check-box is marked, international preliminary examination will start on the basis of the international application as originally filed or, where a copy of amendments to the claims under Article 19 and/or amendments to the international application under Article 34 are received by the International Preliminary Examining Authority before it has begun to draw up a written opinion or the international preliminary examination report, as so amended.

Box No. V ELECTION OF STATES

The applicant hereby elects all eligible States except

Box No. VI CHECK LIST

The demand is accompanied by the following documents for the purposes of international preliminary examination:

| | | | For international Preliminary Examining Authority use only | |
|---|---|----------|--|--------------------------|
| | | | received | not received |
| 1. amendments under Article 34 | : | sheets | <input type="checkbox"/> | <input type="checkbox"/> |
| description | : | sheets | <input type="checkbox"/> | <input type="checkbox"/> |
| claims | : | sheets | <input type="checkbox"/> | <input type="checkbox"/> |
| drawings | : | sheets | <input type="checkbox"/> | <input type="checkbox"/> |
| letter accompanying amendments under Article 34 | : | sheets | <input type="checkbox"/> | <input type="checkbox"/> |
| 3. copy of amendments under Article 19 | : | sheets | <input type="checkbox"/> | <input type="checkbox"/> |
| 4. copy of statement under Article 19 | : | sheets | <input type="checkbox"/> | <input type="checkbox"/> |
| 5. other (specify): Letter requesting detailed preliminary examination | : | 1 sheets | <input type="checkbox"/> | <input type="checkbox"/> |

The demand is also accompanied by the item(s) marked below:

- | | | |
|--|-------------------------------------|--------------------------------|
| 1. <input checked="" type="checkbox"/> separate signed power of attorney | <input checked="" type="checkbox"/> | fee calculation sheet |
| 2. <input checked="" type="checkbox"/> copy of general power of attorney | <input checked="" type="checkbox"/> | other (specify): bank transfer |
| 3. <input type="checkbox"/> statement explaining lack of signature | | |

Box No. VII SIGNATURE OF APPLICANT, AGENT OR COMMON REPRESENTATIVE



Haim Chechik

For International Preliminary Examining Authority use only

1 Date of actual receipt of DEMAND:

Adjusted date of receipt of demand due to CORRECTIONS under Rule 60.1(b):

- | | | |
|--|--------------------------|--|
| 3. <input type="checkbox"/> The date of receipt of the demand is AFTER the expiration of 19 months from the priority date and item 4 or 5, below, does not apply. | <input type="checkbox"/> | The applicant has been informed accordingly. |
| 4. <input type="checkbox"/> The date of receipt of the demand is WITHIN the period of 19 months from the priority date as extended by virtue of Rule 80.5. | | |
| 5. <input type="checkbox"/> Although the date of receipt of the demand is after the expiration of 19 months from the priority date, the delay in arrival is EXCUSED pursuant to Rule 82. | | |

For International Bureau use only

Demand received from IPEA on:

PCT REQUEST

Original (for SUBMISSION) - printed on 21.01.2003 03:26:20 PM

| | | |
|--------------|--|---|
| 0 | For receiving Office use only | |
| 0-1 | International Application No. | |
| 0-2 | International Filing Date | |
| 0-3 | Name of receiving Office and "PCT International Application" | |
| 0-4 | Form - PCT/RO/101 PCT Request | |
| 0-4-1 | Prepared using | PCT-EASY Version 2.92 (updated 01.01.2003) |
| 0-5 | Petition The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty | |
| 0-6 | Receiving Office (specified by the applicant) | Israel Patent Office (RO/IL) |
| 0-7 | Applicant's or agent's file reference | 14128/WO/02 |
| I | Title of invention | NEW FIRE RETARDANTS |
| II | Applicant | |
| II-1 | This person is: | applicant only |
| II-2 | Applicant for | all designated States except US |
| II-4 | Name | BROMINE COMPOUNDS LTD. |
| II-5 | Address: | Makleff House P.O. Box 180 84101 Beer-Sheva Israel |
| II-6 | State of nationality | IL |
| II-7 | State of residence | IL |
| III-1 | Applicant and/or inventor | |
| III-1-1 | This person is: | applicant and inventor |
| III-1-2 | Applicant for | US only |
| III-1-4 | Name (LAST, First) | ZILBERMAN, Joseph |
| III-1-5 | Address: | 13/2 Bat Chen Street 32990 Haifa Israel |
| III-1-6 | State of nationality | IL |
| III-1-7 | State of residence | IL |

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| | | |
|--------------|----------------------------------|---|
| III-2 | Applicant and/or inventor | |
| III-2-1 | This person is: | applicant and inventor |
| III-2-2 | Applicant for | US only |
| III-2-4 | Name (LAST, First) | TAVOR, Alon |
| III-2-5 | Address: | 111 Eucalyptus Street 84965 Omer Israel |
| III-2-6 | State of nationality | IL |
| III-2-7 | State of residence | IL |
| III-3 | Applicant and/or inventor | |
| III-3-1 | This person is: | applicant and inventor |
| III-3-2 | Applicant for | US only |
| III-3-4 | Name (LAST, First) | CANFI, Dorit |
| III-3-5 | Address: | 61 Netiv Chen Street Neve Sha'anana 32687 Haifa Israel |
| III-3-6 | State of nationality | IL |
| III-3-7 | State of residence | IL |
| III-4 | Applicant and/or inventor | |
| III-4-1 | This person is: | applicant and inventor |
| III-4-2 | Applicant for | US only |
| III-4-4 | Name (LAST, First) | IOFFE, David |
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| III-4-7 | State of residence | IL |
| III-5 | Applicant and/or inventor | |
| III-5-1 | This person is: | applicant and inventor |
| III-5-2 | Applicant for | US only |
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| III-5-6 | State of nationality | IL |
| III-5-7 | State of residence | IL |

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| | | |
|--------------|--|--|
| III-6 | Applicant and/or inventor | |
| III-6-1 | This person is: | applicant and inventor |
| III-6-2 | Applicant for | US only |
| III-6-4 | Name (LAST, First) | BRON, Samuel |
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| III-6-6 | State of nationality | IL |
| III-6-7 | State of residence | IL |
| III-7 | Applicant and/or inventor | |
| III-7-1 | This person is: | applicant and inventor |
| III-7-2 | Applicant for | US only |
| III-7-4 | Name (LAST, First) | WEINBERG, Olga |
| III-7-5 | Address: | 18/23 Abba Hillel Silver Street 32694 Haifa Israel |
| III-7-6 | State of nationality | IL |
| III-7-7 | State of residence | IL |
| IV-1 | Agent or common representative; or address for correspondence The person identified below is hereby/has been appointed to act on behalf of the applicant(s) before the competent International Authorities as: | agent |
| IV-1-1 | Name (LAST, First) | LUZZATTO, Kfir |
| IV-1-2 | Address: | P.O. Box 5352 84152 Beer-Sheva Israel |
| IV-1-3 | Telephone No. | +972-8-6467070 |
| IV-1-4 | Faxsimile No. | +972-8-6467080 |
| IV-1-5 | e-mail | kfir@luzzatto.co.il |
| IV-2 | Additional agent(s) | additional agent(s) with same address as first named agent |
| IV-2-1 | Name(s) | LUZZATTO, Edgar; LUZZATTO, Esther; HACKMEY, Michal; FUERST, Zadok; MANZUROLA, Emanuel; SERUYA, Yehuda; CHECHIK, Haim; BEN-HORIN, Hevion; PRICE, Eyal; SHALEV, Ronit; HACKMEY, Miriam; ZRIHAN-LICHT, Sheila; JACOBSON, Zvi-Michael |

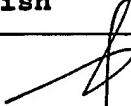
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| | | |
|--------|---|---|
| V | Designation of States | |
| V-1 | Regional Patent (other kinds of protection or treatment, if any, are specified between parentheses after the designation(s) concerned) | AP: GH GM KE LS MW MZ SD SL SZ TZ UG ZM ZW and any other State which is a Contracting State of the Harare Protocol and of the PCT EA: AM AZ BY KG KZ MD RU TJ TM and any other State which is a Contracting State of the Eurasian Patent Convention and of the PCT EP: AT BE BG CH&LI CY CZ DE DK EE ES FI FR GB GR HU IE IT LU MC NL PT SE SI SK TR and any other State which is a Contracting State of the European Patent Convention and of the PCT OA: BF BJ CF CG CI CM GA GN GQ GW ML MR NE SN TD TG and any other State which is a member State of OAPI and a Contracting State of the PCT |
| V-2 | National Patent (other kinds of protection or treatment, if any, are specified between parentheses after the designation(s) concerned) | AE AG AL AM AT AU AZ BA BB BG BR BY BZ CA CH&LI CN CO CR CU CZ DE DK DM DZ EC EE ES FI GB GD GE GH GM HR HU ID IL IN IS JP KE KG KP KR KZ LC LK LR LS LT LU LV MA MD MG MK MN MW MX MZ NO NZ OM PH PL PT RO RU SC SD SE SG SK SL TJ TM TN TR TT TZ UA UG US UZ VC VN YU ZA ZM ZW |
| V-5 | Precautionary Designation Statement In addition to the designations made under items V-1, V-2 and V-3, the applicant also makes under Rule 4.9(b) all designations which would be permitted under the PCT except any designation(s) of the State(s) indicated under item V-6 below. The applicant declares that those additional designations are subject to confirmation and that any designation which is not confirmed before the expiration of 15 months from the priority date is to be regarded as withdrawn by the applicant at the expiration of that time limit. | |
| V-6 | Exclusion(s) from precautionary designations NONE | |
| VI-1 | Priority claim of earlier national application | |
| VI-1-1 | Filing date | |
| VI-1-2 | Number | |
| VI-1-3 | Country | |
| | 31 January 2002 (31.01.2002) | |
| | 147945 | |
| | IL | |

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| | | | |
|--------|---|---|------------------------------------|
| VI-2 | Priority document request The receiving Office is requested to prepare and transmit to the International Bureau a certified copy of the earlier application(s) identified above as item(s): | VI-1 | |
| VII-1 | International Searching Authority Chosen | European Patent Office (EPO) (ISA/EP) | |
| VIII | Declarations | Number of declarations | |
| VIII-1 | Declaration as to the identity of the inventor | - | |
| VIII-2 | Declaration as to the applicant's entitlement, as at the international filing date, to apply for and be granted a patent | - | |
| VIII-3 | Declaration as to the applicant's entitlement, as at the international filing date, to claim the priority of the earlier application | - | |
| VIII-4 | Declaration of inventorship (only for the purposes of the designation of the United States of America) | - | |
| VIII-5 | Declaration as to non-prejudicial disclosures or exceptions to lack of novelty | - | |
| IX | Check list | number of sheets | electronic file(s) attached |
| IX-1 | Request (including declaration sheets) | 6 | - |
| IX-2 | Description | 16 | - |
| IX-3 | Claims | 4 | - |
| IX-4 | Abstract | 1 | EZABST00.TXT |
| IX-5 | Drawings | 0 | - |
| IX-7 | TOTAL | 27 | |
| | Accompanying items | paper document(s) attached | electronic file(s) attached |
| IX-8 | Fee calculation sheet | ✓ | - |
| IX-9 | Original separate power of attorney | ✓ | - |
| IX-9 | Original separate power of attorney | ✓ | - |
| IX-9 | Original separate power of attorney | ✓ | - |
| IX-9 | Original separate power of attorney | ✓ | - |
| IX-9 | Original separate power of attorney | ✓ | - |
| IX-9 | Original separate power of attorney | ✓ | - |
| IX-10 | Original general power of attorney | ✓ | - |
| IX-17 | PCT-EASY diskette | - | Diskette |
| IX-19 | Figure of the drawings which should accompany the abstract | | |
| IX-20 | Language of filing of the International application | English | |
| X-1 | Signature of applicant, agent or common representative |  | |
| X-1-1 | Name (LAST, First) | CHECHIK, Haim | |

PCT REQUEST

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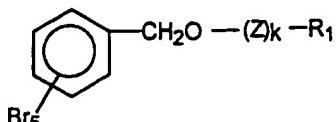
| | | |
|--------|---|--------|
| 10-1 | Date of actual receipt of the purported international application | |
| 10-2 | Drawings: | |
| 10-2-1 | Received | |
| 10-2-2 | Not received | |
| 10-3 | Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application | |
| 10-4 | Date of timely receipt of the required corrections under PCT Article 11(2) | |
| 10-5 | International Searching Authority | ISA/EP |
| 10-6 | Transmittal of search copy delayed until search fee is paid | |

FOR INTERNATIONAL BUREAU USE ONLY

| | | |
|------|--|--|
| 11-1 | Date of receipt of the record copy by the International Bureau | |
|------|--|--|

Claims

1. A pentabromobenzyl alkyl ether of the formula:



wherein:

- Z represents the group $-(\text{Y}-\text{O})_n-$, wherein Y is a linear or branched $-(\text{C}_2-\text{C}_8)\text{alkylene}-$, preferably $-\text{CH}_2\text{CH}_2-$ and $-\text{CH}_2\text{CH}(\text{CH}_3)-$;
- n represents an integer from 2 to 4;
- k may be 0 or 1;
- R_1 represents hydrogen, a linear or branched $-(\text{C}_1-\text{C}_{10})\text{alkyl}$, a linear or branched $-(\text{C}_2-\text{C}_{10})\text{alkylene-OH}$, allyl, or 1,2-dibromopropyl; provided that when k is zero R_1 represents a linear or branched $-(\text{C}_4-\text{C}_{10})\text{alkyl}$ or a linear or branched $-(\text{C}_2-\text{C}_{10})\text{alkylene-OH}$ and when k is 1, R_1 represents hydrogen, a linear or branched $-(\text{C}_1-\text{C}_4)\text{alkyl}$, allyl or 1,2-dibromopropyl.

2. A pentabromobenzyl alkyl ether according to claim 1, wherein Z represents a group selected from $-(\text{C}_2\text{H}_4\text{O})_n$ and $-(\text{C}_3\text{H}_6\text{O})_n$, wherein n represents 1 or 2.

3. A pentabromobenzyl alkyl ether according to claim 1, wherein k=1 and R_1 represents H, methyl or butyl.

4. A pentabromobenzyl alkyl ether according to claim 1, wherein k=0 and R_1 represents branched $(\text{C}_8)\text{alkyl}$ or linear $(\text{C}_6)\text{alkylene-OH}$.

5. A pentabromobenzyl alkyl ether according to claim 1, selected from the group consisting of:

- (i) pentabromobenzyl-O- $\text{CH}_2\text{-CH}_2\text{OCH}_3$;

10/502267

- 16 -

REPLACED BY

ART 34 AMDT

below 15sec. These requirements should be met for both sets of specimens. All the formulations containing the novel pentabromobenzyl alkyl ethers of present invention passed the California TB 117, Section A, Part I test, indicating that they are able to provide a high level of fire retardancy efficiency to flexible polyurethane foams.

Table 3

| Flame retardant | Ether phr | Phosflex 31L phr | Bromine Wt% | Cal 117 RT conditioning | Cal 117 104°C aging |
|--------------------|-----------|------------------|-------------|-------------------------|---------------------|
| None | 0 | | 0 | fail | fail |
| Ether of Example 2 | 8.19 | 2.73 | 3.1 | pass | pass |
| Ether of Example 6 | 8.19 | 2.73 | 3.1 | pass | pass |
| Ether of Example 8 | 8.45 | 2.82 | 3.1 | pass | pass |
| Ether of Example 9 | 8.19 | 2.73 | 3.1 | pass | pass |

While the invention has been described herein above with regard to certain illustrative, specific embodiments, it should be pointed out that many modifications and variations are possible in the light of the above teaching. It is understood therefore, that the invention may be practiced otherwise than as specifically described without departing from the spirit and scope of the invention.

Corrected Version / Version Corrigée

PCT

**NOTICE INFORMING THE APPLICANT OF THE
COMMUNICATION OF THE INTERNATIONAL
APPLICATION TO THE DESIGNATED OFFICES**

(PCT Rule 47.1(c), first sentence)

From the INTERNATIONAL BUREAU

To:

Rec'd PCT/PTO 22 JUL 2004

LUZZATTO, Kfir
P.O. Box 5352
84152 Beer-Sheva
ISRAËL

10/502267

| | | | |
|--|---|---|--|
| Date of mailing(day/month/year) 07 August 2003 (07.08.03) | | | |
| Applicant's or agent's file reference 14128/WO/02 | | IMPORTANT NOTICE | |
| International application No. PCT/IL03/00058 | International filing date(day/month/year) 23 January 2003 (23.01.03) | Priority date(day/month/year) 31 January 2002 (31.01.02) | |
| Applicant BROMINE COMPOUNDS LTD. | | | |

1. Notice is hereby given that the International Bureau has communicated, as provided in Article 20, the international application to the following designated Offices on the date indicated above as the date of mailing of this notice:

AU, AZ, BY, CH, CO, DE, DZ, GH, HU, KG, KP, KR, MD, MK, MZ, RU, TM, US

In accordance with Rule 47.1(c), third sentence, those Offices will accept the present notice as conclusive evidence that the communication of the international application has duly taken place on the date of mailing indicated above and no copy of the international application is required to be furnished by the applicant to the designated Office(s).

2. The following designated Offices have waived the requirement for such a communication at this time:

AE, AG, AL, AM, AP, AT, BA, BB, BG, BR, BZ, CA, CN, CR, CU, CZ, DK, DM, EA, EC, EE, EP, ES, FI, GB, GD, GE, GM, HR, ID, IL, IN, IS, JP, KE, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MG, MN, MW, MX, NO, NZ, OA, OM, PH, PL, PT, RO, SC, SD, SE, SG, SK, SL, TJ, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW

The communication will be made to those Offices only upon their request. Furthermore, those Offices do not require the applicant to furnish a copy of the international application (Rule 49.1(a-bis)).

3. Enclosed with this notice is a copy of the international application as published by the International Bureau on
07 August 2003 (07.08.03) under No. 03/064361

4. **TIME LIMITS for filing a demand for international preliminary examination and for entry into the national phase**

The applicable time limit for entering the national phase will, subject to what is said in the following paragraph, be **30 MONTHS** from the priority date, not only in respect of any elected Office if a demand for international preliminary examination is filed before the expiration of 19 months from the priority date, but also in respect of any designated Office, in the absence of filing of such demand, where Article 22(1) as modified with effect from 1 April 2002 applies in respect of that designated Office. For further details, see *PCT Gazette* No. 44/2001 of 1 November 2001, pages 19926, 19932 and 19934, as well as the *PCT Newsletter*, October and November 2001 and February 2002 issues.

In practice, time limits other than the 30-month time limit will continue to apply, for various periods of time, in respect of certain designated or elected Offices. For regular updates on the applicable time limits (20, 21, 30 or 31 months, or other time limit), Office by Office, refer to the *PCT Gazette*, the *PCT Newsletter* and the *PCT Applicant's Guide*, Volume II, National Chapters, all available from WIPO's Internet site, at <http://www.wipo.int/pct/en/index.html>.

For filing a demand for international preliminary examination, see the *PCT Applicant's Guide*, Volume I/A, Chapter IX. Only an applicant who is a national or resident of a PCT Contracting State which is bound by Chapter II has the right to file a demand for international preliminary examination (at present, all PCT Contracting States are bound by Chapter II).

It is the applicant's sole responsibility to monitor all these time limits.

| | |
|---|---|
| The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland | Authorized officer Judith Zahra |
| Facsimile No.(41-22) 740.14.35 | Telephone No.(41-22) 338.91.11 |

01502267

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau(43) International Publication Date
7 August 2003 (07.08.2003)

PCT

(10) International Publication Number
WO 03/064361 A1(51) International Patent Classification⁷: C07C 43/174, 43/178, C09K 21/08

(74) Agents: LUZZATTO, Kfir et al.; P.O. Box 5352, 84152 Beer-Sheva (IL).

(21) International Application Number: PCT/IL03/00058

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(22) International Filing Date: 23 January 2003 (23.01.2003)

(25) Filing Language: English

(26) Publication Language: English

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(54) Title: PENTABROMOBENZYL ALKYL ETHERS AND THEIR USE AS FIRE RETARDANTS

(57) Abstract: The present invention provides novel pentabromobenzyl alkyl ethers serving as highly effective flame retardants in polymers. The invention further provides a fire retarded polymer composition comprising said pentabromobenzyl alkyl ethers.

PENTABROMOBENZYL ALKYL ETHERS AND THEIR USE AS FIRE RETARDANTS**Field of the Invention**

The present invention provides novel pentabromobenzyl alkyl ethers serving as highly effective flame retardants in polymers. The invention further provides a fire retarded polymer composition comprising said pentabromobenzyl alkyl ethers. The terms fire retardants and flame retardants are used herein synonymously.

Background of the Invention

Compounds containing a pentabromobenzyl moiety are known to be flame retardants. Pentabromobenzyl acrylate (EP 481126), pentabromobenzyl terephthalate (DE 33 20 333), and pentabromobenzyl tetrabromophthalate (EP 47866) are reported to be used in flame retardant polymer compositions. All the above mentioned compounds are esters of carboxylic acids. It is generally known that the ester group is rather unstable to hydrolysis, especially in the presence of acids and bases. This hydrolytic decomposition of esters precludes their use in a great number of applications.

While it is generally recognized that compositions containing bromine improve the flame retardancy of polymers, many bromine-containing compounds are unsatisfactory due to their instability. Such compounds are known to undergo dehydrobromination when incorporated in polymers.

Therefore there is a demand for fire retardants retaining their stability against hydrolysis, especially in the presence of acids and bases. In addition, there is a demand for bromine-containing fire retardants having stability against dehydrobromination when incorporated in polymers.

- 2 -

It is an object of present invention to provide a bromine-containing fire retardant, which has excellent fire-retardancy properties.

It is another object of present invention to provide such fire retardant retaining its stability against hydrolysis and/or decomposition in the presence of an acid or a base.

It is yet a further object of present invention to provide such fire retardant eliminating the undesired dehydrobromination process when incorporated in polymers.

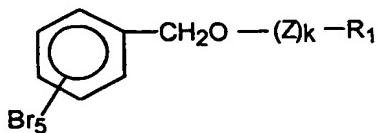
It is yet a further object of present invention to provide fire retarded polymeric and polymer-containing compositions comprising such bromine-containing fire retardant.

The present invention provides novel pentabromobenzyl alkyl ethers possessing highly satisfactory flame retarding characteristics (properties) while retaining their stability against undesired processes, such as dehydrobromination and hydrolysis. The invention further provides polymeric and polymer-containing compositions containing the said novel pentabromobenzyl alkyl ethers that exhibit excellent fire retardancy.

Other objects and advantages of the invention will become apparent as the description proceeds.

Summary of the Invention

The present invention provides a novel pentabromobenzyl alkyl ether of the formula:



wherein:

- Z represents the group $-(Y-O)_n-$, wherein Y is a linear or branched $-(C_2-C_8)alkylene-$, preferably $-CH_2CH_2-$ and $-CH_2CH(CH_3)-$;
- n represents an integer from 2 to 4;
- k may be 0 or 1;
- R_1 represents hydrogen, a linear or branched $-(C_1-C_{10})alkyl$, a linear or branched $-(C_2-C_{10})alkylene-OH$, allyl, or 1,2-dibromopropyl; provided that when k is zero R_1 represents a linear or branched $-(C_4-C_{10})alkyl$ or a linear or branched $-(C_2-C_{10})alkylene-OH$ and when k is 1, R_1 represents hydrogen, a linear or branched $-(C_1-C_4)alkyl$, allyl or 1,2-dibromopropyl.

It further provides a process for the preparation of said novel compounds by the reaction of aliphatic mono- or di-alcohols or the corresponding metal alcoholates with pentabromobenzyl halide, preferably bromide. The pentabromobenzyl alkyl ethers of this invention possess good hydrolytic and thermal stability and are useful as flame retardants in thermoplastic and thermosetting resins. The present invention further provides a fire retarded polymeric and polymer-containing compositions comprising said novel pentabromobenzyl alkyl ethers.

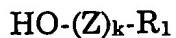
All the above and other characteristics and advantages of the invention will be better understood through the following illustrative and non-limitative detailed description of the preferred embodiments thereof.

Detailed Description of Preferred Embodiments

The pentabromobenzyl alkyl ethers of the present invention are prepared by the reaction of pentabromobenzyl halide, preferably bromide (PBBBr) with

an aliphatic mono- or di-alcohol (or the corresponding metal alcoholate), in the presence or absence of a base.

Aliphatic alcohols (or the corresponding metal alcoholates) which are reacted with pentabromobenzyl halide, preferably PBBBr, to obtain the pentabromobenzyl alkyl ethers of present invention may be represented by the formula:



wherein Z, R₁ and k are as defined above.

Aliphatic alcohols of the above formula used in the process for preparing the compounds of present invention include, *inter alia*, glycols such as ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, propylene glycol, dipropylene glycol, tripropylene glycol, tetrapropylene glycol, and monoethers of these glycols such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl and allyl ether. Other aliphatic alcohols used in said process may be straight chained and branched alcohols such as butanols, pentanols, hexanols, octanols, nonanols, decanols.

Aliphatic di-alcohols also applicable, for example 1,3-propane diol, 1,4-butane diol, 1,5-pentane diol, 1,6-hexane diol, 1,7-heptane diol, 1,8-octane diol, 1,9-nonane diol, 1,10-decane diol.

In a preferred embodiment the reaction of PBBBr and the aliphatic alcohol is carried out in the presence of a strong base such as sodium hydroxide or potassium hydroxide, in a medium of either an organic solvent or an excess aliphatic alcohol. The organic solvent is selected from aromatic compounds. Especially suitable aromatic solvents are chlorobenzene, ortho-dichlorobenzene, bromobenzene, mesitylene, and in particular, toluene and xylene.

An effective amount of the base employed in the process is in a range of 1-1.5 mol per 1 mol PBBBr, and preferably 1-1.2 mol.

When an aromatic solvent is used, the amount of a glycol monoether of the formula HO-(Z)_k-R₁, wherein Z represents -(Y-O)_n-, or of an alcohol in which k is zero, may be in the range of 1-4 mol alcohol, and preferably between 1.5-3 mol, per 1 mol PBBBr.

When the reaction is carried out in an excess of reacting alcohol of the formula HO-(Z)_k-R₁ also used as a solvent, the amount of alcohol is preferably expressed in weight percent in relation to the amount of PBBBr. Thus, the excess of alcohol in such cases is from 200 up to 1000% by weight, and preferably 400-700% by weight, over the amount of PBBBr used. An excess of alcohol below 200% by weight makes carrying out the reaction rather cumbersome and problematic due to the difficulty of stirring the highly concentrated suspension of PBBBr in the alcohol. Using an excess of alcohol greater than 1000% by weight over the amount of PBBBr is inexpedient due to the need of recycling a large quantity of alcohol.

Regardless of the presence or absence of the aromatic organic solvent the amount of glycol of the formula HO-(Z)_k-R₁, wherein Z represents -(Y-O)_n-, (R₁ is H and Y and n are as defined above) or dialcohols of the formula HO-(Z)_k-R₁, wherein k is zero and R₁ represents a linear or branched -(C₂-C₁₀)alkylene-OH, comprises between 5-18 mol, and preferably between 10-15 mol per 1 mol PBBBr. The relatively large excessive amounts of these alcohols are required for minimizing the formation of undesirable di-ethers, namely di-pentabromobenzyl ethers of glycols and diols. Using a molar ratio greater than 18 mol alcohol per 1 mol PBBBr is inexpedient due to the need to recycle a larger quantity of alcohol.

Said reactions are carried out at a temperature of between 40 and 150°C, and preferably between 50 and 110°C. Applying a temperature lower than 40°C resulted in a low yield. On the other hand, applying a temperature higher than 150°C is not advisable since at such temperatures undesirable decomposition products are formed in the presence of a strong base.

Sodium or potassium hydroxide is employed in a solid form. Water should be eliminated from the reaction mixture as much as possible. When aqueous solutions of hydroxides are used the main reaction products are pentabromobenzyl alcohol and di-pentabromobenzyl ether.

The reaction may also be conducted without a base. However, due to the fact that PBBBr is considerably less reactive towards alcohols in the absence of a strong base, the reaction must be carried out at a temperature of between 170 and 220°C. Applying such high temperatures favors the formation of undesired decomposition products.

The following examples illustrate specific embodiments of both the preparation of certain compounds of the invention and the utility of these compounds as flame retardants in various polymer resins. The following examples should not be construed as limiting the scope thereof.

Example 1

A 2 liter reactor, equipped with a mechanical stirrer, a thermometer and a reflux condenser, is charged with PBBBr (212g, 0.37mol) and 2-methoxyethanol (700g, 10mol). The slurry formed is heated to 105°C, followed by addition of potassium hydroxide powder (25.7g, 0.39mol). The resulting mixture is heated for 3 hours at 105°C, with vigorous stirring until the PBBBr conversion is complete (confirmed by HPLC analysis). The solids are filtered at room temperature and washed with water (300g) to remove

potassium bromide. After vacuum drying of the remaining solid, there are obtained 182g (83% of theoretical) of 1-methoxy-2-pentabromobenzylloxyethane [pentabromobenzyl-O-CH₂-CH₂OCH₃] in the form of a white solid powder, melting point 145-146°C. HPLC analysis shows the purity to be 100% (area%). The unreacted 2-methoxyethanol is recovered by stripping off the ethanol and can be used repeatedly.

Example 2

A 2 liter reactor, equipped with a mechanical stirrer, a thermometer and a reflux condenser, is charged with PBBBr (500g, 0.88mol), 2-butoxyethanol (212g, 1.8mol) and toluene (800ml). The slurry formed is heated to 55°C, followed by addition of sodium hydroxide powder (38g, 0.9mol). The resulting mixture is heated for 3 hours at 55°C, with vigorous stirring until the PBBBr conversion is complete (confirmed by HPLC analysis). The final reaction mixture is cooled to room temperature, sodium bromide formed is filtered off and the toluene is fully stripped off. The remaining viscous liquid is mixed with ethanol (1l) at 75°C and a by-product constitutes bis(pentabromobenzyl) ether which does not dissolve in ethanol, is removed by hot filtration. After crystallization, filtration and vacuum drying, there is obtained 426g (80% of theoretical) of 1-butoxy-2-pentabromobenzylloxyethane [pentabromobenzyl-O-CH₂CH₂O(CH₂)₃CH₃] in the form of a white solid powder, melting point 67°C. The HPLC analysis shows the purity to be 100% (area%). The unreacted 2-butoxyethanol is recovered by stripping off the ethanol and can be used repeatedly.

Example 3

A 0.25 liter reactor, equipped with a mechanical stirrer, a thermometer, and a reflux condenser, is charged with the monomethyl ether of diethylene glycol (12 g, 0.1 mol), NaOH (1.6g, 0.038 mol) and ortho-xylene (80ml). The reactor contents are heated to 70°C, followed by addition of PBBBr (20g,

0.035mol). The resulting mixture is heated for 2 hours at 70°C with vigorous stirring until the PBBBr conversion is complete (HPLC analysis). The treatment of the final reaction mixture is carried out as described in Example 1. There is obtained 15.9g (75% of theoretical) of 1-(pentabromophenyl)-2,5,8-trioxanonane [pentabromobenzyl-O-(CH₂CH₂O)₂CH₃] in the form of a white solid powder, melting point 83°C. HPLC analysis shows the purity to be 99.5% (area%).

Example 4

A 2 liter reactor, equipped with a mechanical stirrer, a thermometer, and a reflux condenser, is charged with diethylene glycol (637g, 6 mol) and solid sodium hydroxide (16.8g, 0.42 mol). The mixture is heated to 80°C, followed by portion-wise addition of PBBBr (226.2g, 0.4mol) over a period of 1.5 h. The reaction slurry is heated for one more hour with vigorous stirring until the PBBBr conversion is complete (confirmed by HPLC analysis). Ethanol (0.75 l) is added and the precipitated solid is washed thoroughly with 1l of 50% aq. ethanol. After vacuum drying there is obtained 217g (92% of theoretical) of 3,6-dioxa-7-(pentabromophenyl)-heptanol-1[pentabromobenzyl-O-(CH₂CH₂O)₂H] in the form of a white solid, melting point 117-120°C. HPLC analysis shows the purity to be 98% (area%). The product contains 2% diethylene glycol dipentabromobenzyl ether.

Example 5

A 2 liter reactor, equipped with a mechanical stirrer, a thermometer and a reflux condenser, is charged with PBBBr (453g, 0.8mol) and 1,6-hexane diol (1134g, 9.6mol). The slurry formed is heated to 85°C, followed by addition of sodium hydroxide powder (36g, 0.88mol). The resulting mixture is heated at 85°C for 4 hours with vigorous stirring until the PBBBr conversion is complete (confirmed by HPLC analysis). The excess diol is distilled off under vacuum (1 mm Hg, 100-105°C) and can be used repeatedly. The residue is

treated with refluxing acetonitrile (1l) followed by hot filtration to remove sodium bromide and bis(pentabromobenzyl) ether. After crystallization, filtration and vacuum drying there is obtained 337g (70% of theoretical) of 6-(pentabromobenzylloxy)- hexanol-1 [pentabromobenzyl-O-(CH₂)₆OH] in the form of a white solid powder, melting point 81-83°C. HPLC analysis shows the purity to be 98% (area%).

Example 6

A 1 liter reactor, equipped with a mechanical stirrer, a thermometer and a reflux condenser, is charged with 2-ethylhexanol-1 (68.3g, 0.525mol), toluene (400ml) and potassium hydroxide (17.3g, 0.26mol). The reactor contents are heated to 90°C, followed by addition of PBBBr (102g, 0.18mol). The reaction mixture is heated for 5 hours at 90°C with vigorous stirring until the PBBBr conversion is complete (confirmed by HPLC analysis). The final reaction mixture is cooled to room temperature, sodium bromide is filtered off and the toluene is fully stripped. The remaining viscous liquid is mixed with 0.15 l ethanol-water (80:20) at 75°C and bis(pentabromobenzyl) ether is removed by hot filtration. After crystallization in an ice bath, filtration and vacuum drying there is obtained 88.7g (80% of theoretical) of pentabromobenzyl 2-ethylhexyl ether [pentabromobenzyl-O-CH₂CH(C₂H₅)-(CH₂)₃CH₃]. The final product is in the form of a white wax at room temperature. HPLC analysis shows the purity to be 99% (area%).

Example 7

A 0.25 liter reactor, equipped with a mechanical stirrer, a thermometer, a reflux condenser and a Dean-Stark trap, is charged with 2-allyloxyethanol (7.2g, 0.07mol), toluene (100ml) and sodium hydroxide (1.5g, 0.037mol). The reactor contents are heated to reflux and the water formed is removed as an azeotrop with toluene. After cooling down of the reactor contents to 90°C PBBBr (20g, 0.035mol) is added and after heating at 90°C for 1 hour the

PBBBr conversion is complete (confirmed by HPLC analysis). The final reaction mixture is cooled to room temperature, sodium bromide is filtered off and the toluene is fully stripped. The crystallization of the residue from ethanol-dichloroethane (3:1) affords 16.8g (81% of theoretical) of 1-allyloxy-2-pentabromobenzyl ether [pentabromobenzyl-O-CH₂CH₂OCH₂CH=CH₂] in the form of a beige solid powder, melting point 87-88°C. HPLC analysis shows the purity to be 99.6% (area%).

Example 8

A 0.25 liter reactor, equipped with a mechanical stirrer, a thermometer, a reflux condenser and a Dean-Stark trap connected to a vacuum pump, is charged with monomethyl ether of dipropylene glycol (26.6g, 0.18mol), toluene (100ml) and sodium hydroxide (4g, 0.1mol). The reactor contents are heated to reflux (105°C) under a reduced pressure of 810 mbar and the water formed is removed as an azeotrope with toluene. The reactor contents are cooled down while refluxing by gradually reducing the pressure to 65 mbar. When the temperature is 35°C the pressure in the reactor is allowed to equalize to atmospheric pressure, and PBBBr (50 g, 0.088mol) is added. The reaction mixture is heated at 70°C for 2 hours, with vigorous stirring, until no PBBBr is detected (HPLC analysis). The reaction mixture is cooled to room temperature and neutralized to pH 7 with concentrated hydrochloric acid. The sodium bromide formed is filtered off and the toluene is fully stripped. The excess monomethyl ether of dipropylene glycol is distilled off at 80-120°C (15 mbar). The hot mixture is filtered to remove traces of the by-product bis(pentabromobenzyl) ether. The residue is washed twice with 50 ml water at 70°C. After vacuum drying 51.5 g (92% yield) of dipropylene glycol methyl pentabromobenzyl ether [pentabromobenzyl-O-(C₃H₆O)₂CH₃] is obtained in the form of a clear amber liquid. HPLC analysis shows the purity to be above 99% (area%). The product is a mixture of isomers.

Example 9

A 2 liter reactor, equipped with a mechanical stirrer, a thermometer, and a reflux condenser attached to a Dean-Stark trap, is charged with dipropylene glycol (322g, 2.4mol), toluene (600ml) and sodium hydroxide (18g, 0.44mol). The reactor contents are heated to reflux and the water formed is removed as an azeotrope with toluene. After cooling the reactor contents to 50°C, PBBBr (226g, 0.4mol) is added. The reaction mixture is heated at 70°C for 2 hours, with vigorous stirring, until no PBBBr is detected (HPLC analysis). The final reaction mixture is cooled to room temperature and neutralized to pH 7 with concentrated hydrochloric acid. The toluene is fully stripped and the excess dipropylene glycol is then distilled off at 105-108°C (1-2 mbar). The hot liquid residue is washed with 400ml water four times at 80°C, and then filtered to remove traces of bis(pentabromobenzyl)ether. After vacuum drying 220g (90% yield) of dipropylene glycol pentabromobenzyl ether [pentabromobenzyl-O-(C₃H₆O)₂H] is obtained in the form of a beige wax. HPLC analysis shows the purity to be above 99% (area%). The product is a mixture of isomers.

The novel compounds of the present invention are highly efficient flame retardants when incorporated into various polymers or polymer-containing compositions. In general, the novel compounds of present invention are useful as flame retardants in a wide variety of polymeric compositions such as, for example, chlorinated polyethylene, polyethylene, polypropylene, styrene resins, high-impact polystyrene, polyvinyl chloride, acrylonitrile-butadiene-styrene copolymer, flexible and rigid polyurethanes, epoxy resins, unsaturated polyester resins and the like. In particular, the compounds of present invention are highly effective flame retardants in polyurethanes. The novel compounds of the invention are also useful as fire retardants when incorporated into polymer-containing compositions. Such compositions as used herein are polymeric compositions that also comprise other constituents (other than the fire retardants of the invention). Such

constituents may be, but are not limited to, catalysts, antioxidants, anti-dripping agents and the like. In the polymer-containing compositions the polymeric constituent may be any one of the above-mentioned polymers.

The amount of novel compound of present invention which is necessary for conferring commercially satisfactory flame retardancy to a particular polymer or polymer-containing composition may vary over a wide range. Usually, the flame retardant material of present invention is employed in an amount of between about 1 to 50% by weight of the polymer. Preferably, between about 3 to about 30% is used. In general, any suitable known method of incorporating flame retardants to polymer materials may be employed.

The following examples demonstrate the utility of the pentabromobenzyl alkyl ether of the present invention as a flame retardant in various polymers.

Example 10

In this example polypropylene (block copolymer of polypropylene with propylene-ethylene rubber, Capilene SG-50, a trade mark of Carmel Olefins) in a granulated form was used as the polymer resin. Different pentabromobenzyl alkyl ethers, each in amount corresponding to 22wt% of bromine and 11wt% of antimony oxide as a synergist, were admixed with the polypropylene. Regular amounts of antioxidants and anti-dripping agents, when applied, were added to the mixture at the expense of the polymer. Mixing was done in a Brabender internal mixer of 55cm³ volume capacity at 50 rotations per minute and 190°C for various periods. Specimens of 3.2mm thickness were prepared by compression molding in a hot press at 200°C, cooling to room temperature and cutting into standard test pieces.

The flammability was tested by the limiting oxygen index method (hereinafter referred to as "LOI") in accordance with ASTM D-2863-99. LOI is defined as the minimum concentration of oxygen (%vol) in a mixture of oxygen and nitrogen that will just support combustion of the fire retarded polymer under the conditions of the test procedure. The utility of pentabromobenzyl alkyl ethers as flame retardants is shown in Table 1: all formulations containing pentabromobenzyl alkyl ethers have a significantly larger LOI than the neat polymer.

Table 1

| Flame retardant* | Wt.% | LOI, O ₂ % |
|--------------------|------|-----------------------|
| None | 0.0 | 16.7 |
| Ether of Example 1 | 30.8 | 23.5 |
| Ether of Example 2 | 33.7 | 23.0 |
| Ether of Example 5 | 34.4 | 22.8 |
| Ether of example 6 | 33.7 | 22.0 |

* Each formulation contains 22wt% bromine

Example 11

In this example, polystyrene (either a High Impact Polystyrene (HIPS) - Styron 472, a trade mark of Dow, or a Acryl-Butadiene-Styrene terpolymer (ABS) - Magnum 3404, a trade mark of General Electric) was used as the polymer resin. Different pentabromobenzyl alkyl ethers in various amounts corresponding to a bromine content of 6%, 11% or 12%, and antimony oxide as a synergist, as shown in Table 2, were admixed with the polymer in a granulated form. Regular amounts of antioxidants and anti-dripping agents, when applied, were added to the mixture at the expense of the polymer. Mixing was done in a Brabender internal mixer of 55 cm³ volume capacity at 50 rotations per minute and 200°C for the desired time. Specimens of 3.2mm or 1.6mm thickness were prepared by compression molding in a hot press at

200°C, cooling to room temperature and cutting into standard test pieces. The flammability was tested by the limiting oxygen index method (as described above) in accordance with ASTM D-2863, and by the UL-94 test (Underwriters Laboratories) with bottom ignition for two successive 10-second intervals by a standard burner flame. Five test-pieces of each composition were tested under the conditions of the UL-94 procedure. A wide range of flame retardancy of styrene polymers can be achieved (UL-94 rating V-2 or V-0) at 1.6 and 3.2mm thickness, indicating that the novel pentabromobenzyl alkyl ethers of present invention provides a high level of fire retardancy efficiency.

Table 2

| Flame retardant | Polymer type | Ether Wt% | Bromine Wt% | Sb ₂ O ₃ Wt% | LOI O ₂ % | UL-94 3.2mm | UL-94 1.6mm |
|--------------------|--------------|-----------|-------------|------------------------------------|----------------------|-------------|-------------|
| None | ABS | 0 | 0 | 0 | 18.0 | NR | NR |
| None | HIPS | 0 | 0 | 0 | 17.8 | NR | NR |
| Ether of Example 1 | HIPS | 15.4 | 11.0 | 6.0 | 24.4 | V-0 | |
| | ABS | 15.4 | 11.0 | 6.0 | 24.8 | V-0 | |
| | HIPS | 16.8 | 12.0 | 6.0 | 25.1 | | V-0 |
| Ether of Example 2 | HIPS | 16.9 | 11.0 | 6.0 | 23.8 | V-0 | |
| | HIPS | 9.2 | 6.0 | 3.0 | 21.8 | | V-2 |
| Ether of Example 6 | HIPS | 16.9 | 11.0 | 6.0 | 23.2 | V-0 | |
| | HIPS | 9.2 | 6.0 | 3.0 | 21.4 | | V-2 |
| Ether of Example 5 | HIPS | 17.2 | 11.0 | 6.0 | 24.0 | V-0 | |
| | ABS | 17.2 | 11.0 | 6.0 | 24.8 | V-0 | |
| | HIPS | 18.2 | 12.0 | 6.0 | 24.7 | | V-0 |
| Ether of Example 4 | ABS | 17.9 | 12.0 | 6.0 | - | | V-0 |
| | HIPS | 17.9 | 12.0 | 6.0 | - | | V-0 |

Example 12

In this example, standard flexible polyurethane foam was used as polymeric matrix. Different pentabromobenzyl alkyl ethers were added in various amounts as shown in Table 3. The ethers were added as a 75:25 mixture with an isopropylated triphenyl phosphate ester (Phosflex 31L ex Akzo Nobel). The polyol (100 parts polyol per one hundred parts resin (phr)), water (4.2phr), surfactant (1.1phr), flame retardant and catalysts were weighed and mixed using a high speed mixer at about 3000 rpm. The polyol used in this example was a polyether with terminal hydroxyl groups. The molecular weight was about 4800 and the hydroxyl number was 46 mg KOH/g. TDI (54.8phr) was added under the hood, mixed for 10sec including the pouring time (the timer was started when TDI was added). The TDI is a 80:20 mixture of 2,4- and 2,6 - toluene - diisocyanate. The mixture was then quickly poured into a shoebox with dimensions 33x20x20cm³. The usual cream time (from the moment TDI was added till the foam started to rise) was about 15sec for all formulations. The usual blow off time (measured from the moment TDI was added till the foam stopped rising and CO₂ was suddenly released through the upper surface) was about 130-140 sec. The resulting bun was let to cool under the hood for 24 hours, dismantled from the shoebox and cut into 30x7.5x1.27cm³ specimens. At least 10 specimens were tested, 5 specimens from each formulations after conditioning at room temperature and 50±5% relative humidity for 24 hours, and another set of 5 specimens from each formulation after aging for 24 hours at 104°C. The specimens were subjected to the vertical burning test in a special cabinet as required by the California TB 117, Section A, Part I. The flammability was tested by bottom ignition for a 12-second interval using a vertical burner butane flame with a length of 40mm. For a formulation to pass the test, it is required that the maximum char length would be below 20cm, the average char length below 15cm, the average after-flame time below 5sec, the maximum after-flame time below 10sec, and the maximum after-glow time

below 15sec. These requirements should be met for both sets of specimens. All the formulations containing the novel pentabromobenzyl alkyl ethers of present invention passed the California TB 117, Section A, Part I test, indicating that they are able to provide a high level of fire retardancy efficiency to flexible polyurethane foams.

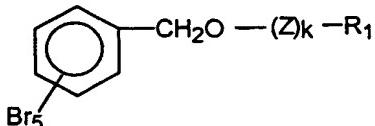
Table 3

| Flame retardant | Ether phr | Phosflex 31L phr | Bromine Wt% | Cal 117 RT conditioning | Cal 117 104°C aging |
|--------------------|-----------|------------------|-------------|-------------------------|---------------------|
| None | 0 | | 0 | fail | fail |
| Ether of Example 2 | 8.19 | 2.73 | 3.1 | pass | pass |
| Ether of Example 6 | 8.19 | 2.73 | 3.1 | pass | pass |
| Ether of Example 8 | 8.45 | 2.82 | 3.1 | pass | pass |
| Ether of Example 9 | 8.19 | 2.73 | 3.1 | pass | pass |

While the invention has been described herein above with regard to certain illustrative, specific embodiments, it should be pointed out that many modifications and variations are possible in the light of the above teaching. It is understood therefore, that the invention may be practiced otherwise than as specifically described without departing from the spirit and scope of the invention.

Claims

1. A pentabromobenzyl alkyl ether of the formula:



wherein:

- Z represents the group $-(\text{Y}-\text{O})_n-$, wherein Y is a linear or branched $-(\text{C}_2-\text{C}_8)\text{alkylene}-$, preferably $-\text{CH}_2\text{CH}_2-$ and $-\text{CH}_2\text{CH}(\text{CH}_3)-$;
- n represents an integer from 2 to 4;
- k may be 0 or 1;
- R_1 represents hydrogen, a linear or branched $-(\text{C}_1-\text{C}_{10})\text{alkyl}$, a linear or branched $-(\text{C}_2-\text{C}_{10})\text{alkylene-OH}$, allyl, or 1,2-dibromopropyl; provided that when k is zero R_1 represents a linear or branched $-(\text{C}_4-\text{C}_{10})\text{alkyl}$ or a linear or branched $-(\text{C}_2-\text{C}_{10})\text{alkylene-OH}$ and when k is 1, R_1 represents hydrogen, a linear or branched $-(\text{C}_1-\text{C}_4)\text{alkyl}$, allyl or 1,2-dibromopropyl.

2. A pentabromobenzyl alkyl ether according to claim 1, wherein Z represents a group selected from $-(\text{C}_2\text{H}_4\text{O})_n$ and $-(\text{C}_3\text{H}_6\text{O})_n$, wherein n represents 1 or 2.

3. A pentabromobenzyl alkyl ether according to claim 1, wherein k=1 and R_1 represents H, methyl or butyl.

4. A pentabromobenzyl alkyl ether according to claim 1, wherein k=0 and R_1 represents branched $(\text{C}_8)\text{alkyl}$ or linear $(\text{C}_6)\text{alkylene-OH}$.

5. A pentabromobenzyl alkyl ether according to claim 1, selected from the group consisting of:

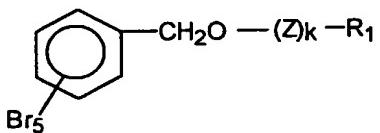
- (i) pentabromobenzyl-O- $\text{CH}_2\text{-CH}_2\text{OCH}_3$;

- (ii) pentabromobenzyl-O-CH₂CH₂O(CH₂)₃CH₃;
- (iii) pentabromobenzyl-O-(CH₂CH₂O)₂CH₃;
- (iv) pentabromobenzyl-O-(CH₂CH₂O)₂H;
- (v) pentabromobenzyl-O-(CH₂)₆OH;
- (vi) pentabromobenzyl-O-CH₂CH(C₂H₅)(CH₂)₃CH₃;
- (vii) pentabromobenzyl-O-CH₂CH₂OCH₂CH=CH₂;
- (viii) pentabromobenzyl-O-(C₃H₆O)₂-CH₃
- (ix) pentabromobenzyl-O-(C₃H₆O)₂-H

6. A compound according to any one of claims 1 to 5, for use as a fire retardant.

7. A compound according to any one of claims 1 to 5, for use as a fire retardant in a polymeric composition or in polymer-containing composition.

8. A fire retarded polymeric or polymer-containing composition comprising a pentabromobenzyl alkyl ether of the formula:



wherein Z, R₁ and k are as defined in claim 1.

9. A fire retarded composition according to claim 8, wherein said polymer is selected from the group consisting of chlorinated polyethylene, polyethylene, polypropylene, styrene resins, high-impact polystyrene, polyvinyl chloride, acrylonitrile-butadiene-styrene copolymer, flexible and rigid polyurethane, epoxy resins and unsaturated polyester resins.

10. A fire retarded composition according to claim 9, wherein said polymer is polypropylene.

11. A fire retarded composition according to claim 9, wherein said polymer is high impact polystyrene (HIPS).

12. A fire retarded composition according to claim 9, wherein said polymer is acryl-butadiene-styrene terpolymer (ABS).

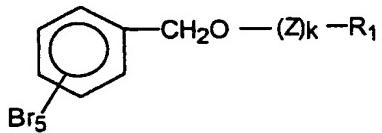
13. A fire retarded composition according to claim 9, wherein said polymer is polyurethane.

14. A fire retarded composition according to claim 8, wherein said polymer is selected from the group consisting of polyurethane, polypropylene copolymer, high impact polystyrene (HIPS) and acryl-butadiene-styrene terpolymer (ABS), and said pentabromobenzyl alkyl ether is selected from the group consisting of:

- (i) pentabromobenzyl-O-CH₂-CH₂OCH₃;
- (ii) pentabromobenzyl-O-CH₂CH₂O(CH₂)₃CH₃;
- (iii) pentabromobenzyl-O-(CH₂CH₂O)₂CH₃;
- (iv) pentabromobenzyl-O-(CH₂CH₂O)₂H;
- (v) pentabromobenzyl-O-(CH₂)₆OH;
- (vi) pentabromobenzyl-O-CH₂CH(C₂H₅)(CH₂)₃CH₃;
- (vii) pentabromobenzyl-O-CH₂CH₂OCH₂CH=CH₂;
- (viii) pentabromobenzyl-O-(C₃H₆O)₂-OCH₃
- (ix) pentabromobenzyl-O-(C₃H₆O)₂-H

15. A fire retarded composition according to any one of claims 8 to 14, further comprising a metal oxide, preferably Sb₂O₃.

16. A process for the preparation of a pentabromobenzyl alkyl ether of the formula:



wherein Z, R₁ and k are as defined in claim 1, comprising reacting a glycol, a mono-, or di-alcohol of the formula HO-(Z)_k-R₁, wherein Z, R₁ and k are as defined in claim 1, or the corresponding metal alcoholate thereof, with a pentabromobenzyl halide, preferably pentabromobenzyl bromide, optionally in the presence of a base.

17. A pentabromobenzyl alkyl ether according to claim 1, for use as a fire retardant, substantially as described and exemplified in the specification.

18. A process for the preparation of pentabromobenzyl alkyl ethers as defined in claim 1, substantially as described and exemplified in the specification.

19. A fire retarded polymer composition comprising pentabromobenzyl alkyl ether according to claim 1, substantially as described and exemplified in the specification.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/03/00058

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C07C43/174 C07C43/178 C09K21/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

CHEM ABS Data, BEILSTEIN Data, EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category ° | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|---|-----------------------|
| X | US 4 119 612 A (VOLLKOMMER NORBERT ET AL) 10 October 1978 (1978-10-10) column 5, line 35 - line 42 column 14 -column 15; example 2 column 18; example 8 column 23; example 16 column 25 -column 28; examples 22-29 --- | 1,3 |
| A | column 5, line 35 - line 42 column 14 -column 15; example 2 column 18; example 8 column 23; example 16 column 25 -column 28; examples 22-29 --- | 2,4-19 |
| A | EP 0 344 700 A (BROMINE COMPOUNDS LTD) 6 December 1989 (1989-12-06) claim 1; examples --- | 1,8 -/- |

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

° Special categories of cited documents :

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Date of the actual completion of the international search

Date of mailing of the international search report

20 May 2003

06/06/2003

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/03/00058

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|---|-----------------------|
| X,P | <p>DATABASE CAPLUS 'Online!' CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; Database accession no. 2002:599223 XP002241771 abstract & SHISHKIN V.N.: "Reactions with 2,3,4,5,6-Pentabromobenzyl Bromide with Alcohols and Alkali Metal Alkoxides" RUSSIAN JOURNAL OF ORGANIC CHEMISTRY, vol. 38, no. 5, 2002, pages 709-712, -----</p> | 1,16,18 |

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 03/00058

| Patent document cited in search report | | Publication date | | Patent family member(s) | | Publication date |
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14128/WO/02

ART 34 AMDT

- 16 -

below 15sec. These requirements should be met for both sets of specimens. All the formulations containing the novel pentabromobenzyl alkyl ethers of present invention passed the California TB 117, Section A, Part I test, indicating that they are able to provide a high level of fire retardancy efficiency to flexible polyurethane foams.

Table 3

| Flame retardant | Ether phr | Phosflex 81L phr | Bromine Wt% | Cal 117 RT conditioning | Cal 117 104°C aging |
|--------------------|-----------|------------------|-------------|-------------------------|---------------------|
| None | 0 | | 0 | fail | fail |
| Ether of Example 2 | 8.19 | 2.73 | 3.1 | pass | pass |
| Ether of Example 6 | 8.19 | 2.73 | 3.1 | pass | pass |
| Ether of Example 8 | 8.45 | 2.82 | 3.1 | pass | pass |
| Ether of Example 9 | 8.19 | 2.73 | 3.1 | pass | pass |

While the invention has been described herein above with regard to certain illustrative, specific embodiments, it should be pointed out that many modifications and variations are possible in the light of the above teaching. It is understood therefore, that the invention may be practiced otherwise than as specifically described in the above Examples without departing from the spirit and scope of the claimed invention.

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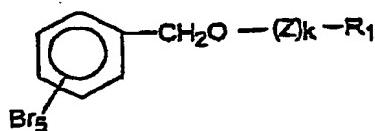
ART 54 AMDT

14128/WO/02

- 17 -

Claims

1. A pentabromobenzyl alkyl ether of the formula:



wherein:

- Z represents the group $-(\text{Y}-\text{O})_n-$, wherein Y is a linear or branched $-(\text{C}_2-\text{C}_8)\text{alkylene}$, preferably $-\text{CH}_2\text{CH}_2-$ and $-\text{CH}_2\text{CH}(\text{CH}_3)-$;
- n represents an integer from 2 to 4;
- k may be 0 or 1;
- R_1 represents hydrogen, a linear or branched $-(\text{C}_1-\text{C}_{10})\text{alkyl}$, a linear or branched $-(\text{C}_2-\text{C}_{10})\text{alkylene-OH}$, allyl, or 1,2-dibromopropyl; provided that when k is zero R_1 represents a linear or branched $-(\text{C}_4-\text{C}_{10})\text{alkyl}$ or a linear or branched $-(\text{C}_2-\text{C}_{10})\text{alkylene-OH}$ and when k is 1, R_1 represents hydrogen, a linear or branched $-(\text{C}_1-\text{C}_4)\text{alkyl}$, allyl or 1,2-dibromopropyl; with the proviso that R_1 is not $-\text{CH}_2\text{-CH}_2\text{-OH}$.
- 2. A pentabromobenzyl alkyl ether according to claim 1, wherein Z represents a group selected from $-(\text{C}_2\text{H}_4\text{O})_n$ and $-(\text{C}_3\text{H}_6\text{O})_n$, wherein n represents 2.
- 3. A pentabromobenzyl alkyl ether according to claim 1, wherein k=1 and R_1 represents H, methyl or butyl.
- 4. A pentabromobenzyl alkyl ether according to claim 1, wherein k=0 and R_1 represents branched $(\text{C}_8)\text{alkyl}$ or linear $(\text{C}_6)\text{alkylene-OH}$.
- 5. A pentabromobenzyl alkyl ether according to claim 1, selected from the group consisting of:
 - (i) pentabromobenzyl-O-CH₂-CH₂OCH₃;

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